

# Photo Double-Ionization of Deuterium Chloride Studied by Threshold Photoelectrons Coincidence Spectroscopy

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## INTRODUCTION

Photo double-ionization (PDI) of DCl has been investigated in the 35-38 eV energy range using synchrotron radiation on beamline 10.0.1.2 of the Advance Light Source (ALS) by the threshold photoelectrons coincidence (TPEsCO) method. The TPEsCO spectrum of DCl, encompassing the formation of the ground ( $X^3\Sigma^-$ ) and first-excited ( $a^1\Delta$ ) states of  $\text{DCl}^{2+}$ , was recorded at good resolution ( $\sim 13$  meV) using a pair of penetrating-field electron spectrometers (see Fig. 1, upper panel). In addition, the threshold photoelectron (TPE) spectrum of DCl for the formation of singly charged DCl was recorded simultaneously in the same energy range (see Fig. 1, lower panel).

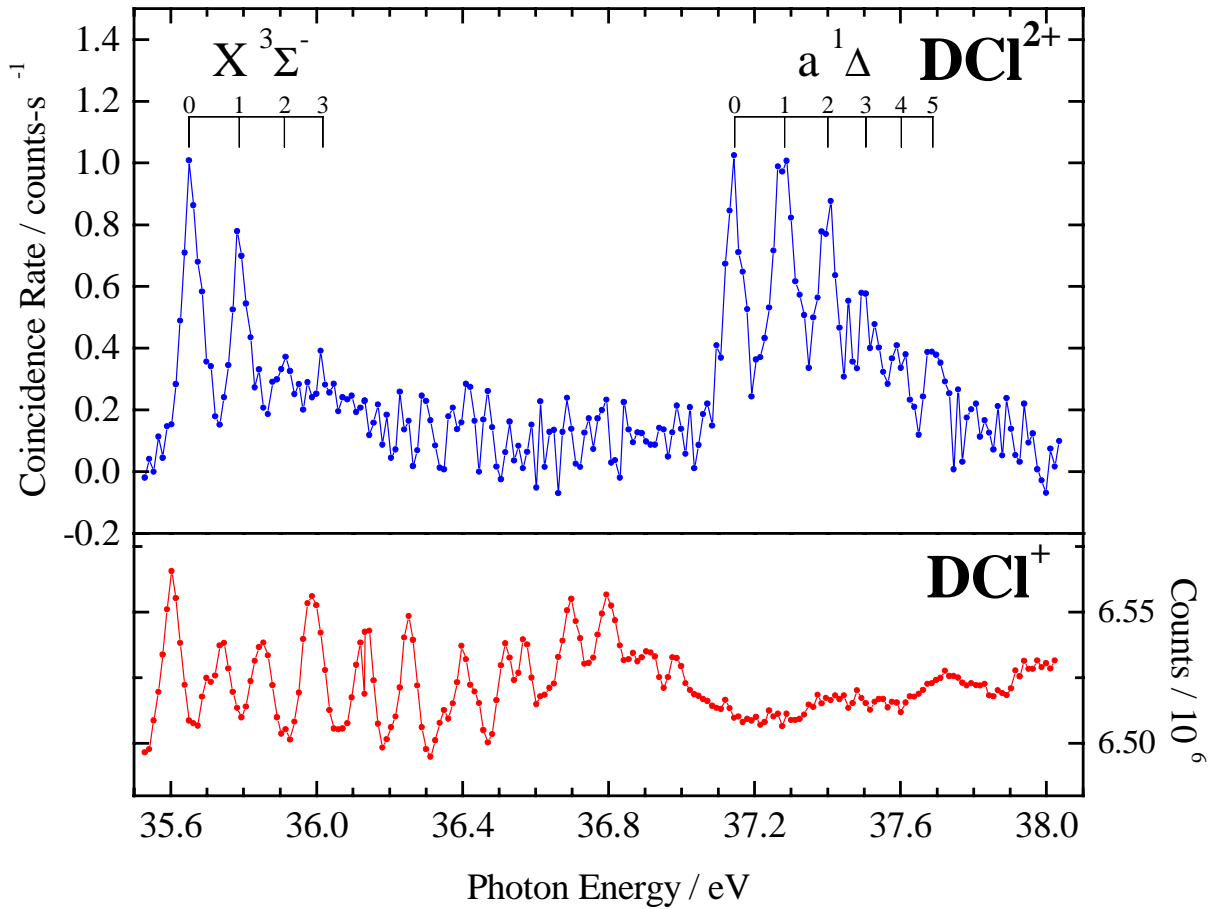


Figure 1. Threshold photoelectrons coincidence spectrum of DCl (upper panel) and threshold photoelectron spectrum of DCl (lower panel).

## RESULTS AND DISCUSSION

As can be seen in the TPEsCO spectrum in Fig. 1 (upper panel) a clear vibrational progression is observed in both systems confirming the TPEsCO results for HCl<sup>1</sup>, thus supporting the quasi-bound nature of these states<sup>2</sup>. The adiabatic double-ionization potentials ( $v^{2+}=0$ ) for these states are found to be 35.650 eV ( $^3\Sigma^-$ ) and 37.145 eV ( $^1\Delta$ ) with an identical vibrational separation ( $v^{2+}=0-1$ ) of 0.137 eV in both systems. The peaks observed in the TPE spectrum in Fig. 1 (lower panel) most probably represent vibrational structure in the formation of satellite DCI<sup>+</sup> ion states converging on one or more excited, doubly-charged DCI states.

The implications of these results are as follows. In the TPEsCO spectrum of DCI the first two vibrational bands in the ( $X\ ^3\Sigma^-$ ) system and the first three vibrational bands in the ( $a\ ^1\Delta$ ) system are intense, well-defined and well-resolved while higher vibrational bands in both systems are much weaker, poorly defined and only barely recognizable as band systems. This suggests that both states are predissociated by tunneling effects, in basic agreement with theoretical calculations on the tunneling lifetimes of the vibrational levels of these states in DCI<sup>2+</sup>.<sup>3</sup> The number of vibrational bands observed in the ( $X\ ^3\Sigma^-$ ) system (four) is supported by theoretical calculations that show<sup>4</sup> that the fifth vibrational level of the DCI<sup>2+</sup> ( $X\ ^3\Sigma^-$ ) state is coincident in energy with the maximum in the potential energy (dissociative) barrier and thereby should not be bound. The observed vibrational intensity distributions within the ( $X\ ^3\Sigma^-$ ) and ( $a\ ^1\Delta$ ) DCI<sup>2+</sup> systems are significantly different from the calculated Franck-Condon factors<sup>3</sup> for direct transitions from the ground state of DCI suggesting an additional route is operative in the TPEsCO spectrum. Such an indirect mechanism is possible by resonance autoionization of singly charged DCI states lying in this energy region as supported by the structured TPE spectrum shown in the lower panel of Fig. 1. The influence of autoionization processes may also be the origin of the structured peaks lying between 36.3 eV and 37.1 eV in the TPEsCO spectrum. Continued analyses of these results are underway and will be compared with the findings in the PDI of HCl.<sup>1</sup>

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## REFERENCES

1. A.G. McConkey, G. Dawer, L. Avaldi, M.A. MacDonald, G.C. King and R.I Hall, J. Phys. B **27**, 271 (1994).
2. F.R. Bennett and I.R. McNab, Chem. Phys. Letters, **251**, 405 (1996) .
3. A. Banichevich, S.D. Peyerimhoff, M.C. Van Hemert and P.G. Fournier, Chem. Phys. **121**, 351 (1988).
4. R. Abusen, F.R. Bennett, I.R. McNab, D.N. Sharp, R.C. Shiell and C.A. Woodward, J. Chem. Phys. **108**, 1761 (1998).

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